Electron Spin Resonance Study of Phosphoranyl Radicals in γ-irradiated CHPCl and (CH)PCl (Special Issue on Physical, Chemical and Biological Effects of Gamma Radiation, XV)

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Note

Electron Spin Resonance Study of Phosphoranyl Radicals in γ-irradiated $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$.

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Electron spin resonance (ESR) spectra of γ-irradiated $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$ have showed clear features of phenylchlorophosphoranyl radicals. Phosphoranyl radicals have been extensively studied by ESR,[1~6] but ESR spectrum of phosphoranyl radical with phenyl substituent has not been reported. The present note describes the identification and some features of phenylchlorophosphoranyl radicals.

Samples of $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$ were irradiated at 77°K in a ^{60}Co source for 10 hours at a dose rate of 0.1 Mrad/h. ESR measurements were carried out at 77°K with JEOL 3BSX and PE-1X spectrometers.

Figure 1 shows the high and low-field components of a doublet ESR spectrum of a radical produced by γ-irradiation of $C_6H_5PCl_2$. This spectrum indicates clearly the presence of a single phosphorus nucleus very strongly coupled with the odd electron (1060 G) and two strongly coupled equivalent chlorine nuclei (53 G). It is widely accepted that phosphoranyl radicals have a trigonal bipyramidal structure with the half-occupied hybrid orbital in the equatorial plane and that the splitting constants of the two axial nuclei are much larger than those of the two equatorial nuclei.[1~6] The hyperfine splitting constants (h.f.s.c.) of tetrachlorophosphoranyl radical ($\dot{P}Cl_4$), formed by γ-irradiation of PCl_3, were reported[3] as a(P)=1214, a(Cl axial)=62, and a(Cl equatorial) =7.5 G. In the analogy to the spectrum of this tetrachlorophosphoranyl radical and its radical formation, we have identified the present radical species as phenyltrichlorophosphoranyl radical ($C_6H_5\dot{P}Cl_3$), in which two chlorine nuclei occupy the axial positions and

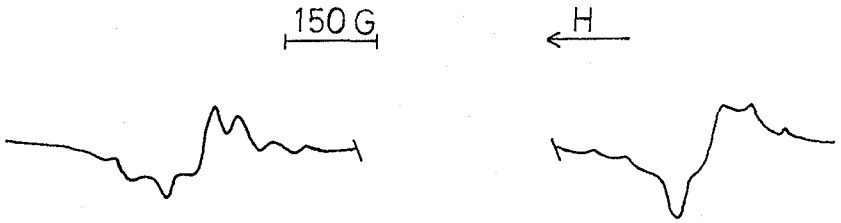

Fig. 1. ESR spectrum of $C_6H_5\dot{P}Cl_3$ in γ-irradiated $C_6H_5PCl_2$ at 77°K.

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Table I. ESR Parameters of $C_6H_5PCl_3$, $(C_6H_5)_2PCl_2$ and Some Related Radicals (G)

Radical	g[a]	a (P)	a (Cl axial)	ρ_{3s} (P)[b]
$\dot{P}Cl_4$[c]	2.013	1214	62	0.33
$CH_3\dot{P}Cl_3$[c]	2.000	1077	—	0.30
$C_6H_5\dot{P}Cl_3$[d]	2.019	1060	53	0.29
$(C_6H_5)_2\dot{P}Cl_2$[d]	2.014	813	59	0.22

[a] Corrected to second order with respect to the hyperfine interactions.
[b] Calculated from the Hartree-Fock value[7] of $a_{3s}(P)=3640$ G.
[c] See Ref. 3.
[d] This work.

the third Cl nucleus and a phenyl ring occupy the equatorial positions, respectively.

Similarly, diphenyldichlorophosphoranyl radical ($(C_6H_5)_2\dot{P}Cl_2$) with the two chlorine nuclei occupying the axial positions was observed in the ESR spectrum of γ-irradiated $(C_6H_5)_2PCl$. The observed ESR parameters of these phosphoranyl radicals are presented in Table I together with some related radicals.

It is generally accepted that the s character of the unpaired electron orbital increases accompanying to the increase of electronegativity of ligand atoms.[3] From this point of view, the data in Table I seems to be reasonable. Namely, the odd electron spin density on 3 s atomic orbital of the phosphorus atom, ρ_{3s} (P), decreases in the order of $\dot{P}Cl_4$ (0.33), $C_6H_5\dot{P}Cl_3$ (0.29), $(C_6H_5)_2\dot{P}Cl_2$ (0.22) as shown in Table I. This fact offers further supports to the present identification of the radicals.

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